A Thermodynamic Perturbation Approach for the Phase Transition Parameters Consistence

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The thermodynamic perturbation method for the phase transition parameter consistence is presented. It is known that the phase transition usually does not occur at the single point of the thermodynamic surface. Instead, the isobaric phase transition extends over a limited range of temperatures and looks like a diffuse transition because of external perturbation influences. The external influences being considered are the selective adsorption on the surface of the experimental cell, the equilibrium admixtures in the bulk phase, and the electric and magnetic fields. The small parameter of the equilibrium perturbation is determined by the comparison of the thermodynamic potentials for both the non-perturbed and the perturbed systems. It is shown that the magnitude of the isobaric phase transition temperature distortion depends on the latent heat of transition and the thermodynamic potential change. The last value is an algebraic sum of the contributions that represent the various external influences. Because these contributions are measured with one common scale, it is possible to compare them with each other and estimate the integrated response of a system to the set of different equilibrium perturbations acting simultaneously.

The influence of non-equilibrium perturbations on the phase transition parameters is estimated in terms of duration of the experiment and the corresponding relaxation time. There is no symmetry of the temperature deviations from the equilibrium temperature for any certain metastable phase. In other words, the non-equilibrium phase transition can be associated with a certain level of the metastability and as a result with a certain time of life of the phase. Due to the positive value of the time of life, these deviations from the equilibrium are allowed in only one direction.

The illustrations and estimations are presented for typical conditions of the thermophysical experiment.